by replacement of another group such as $-OH$ or $-SO_3H$. Examples are:

(1) $C_6H_5-C(H)=CH_2$ + HCl $\xrightarrow{\text{anhydrous}}$ $C_6H_5-C(Cl)-C(Cl)$

(2) benzene + Cl_2 $\xrightarrow[\text{anhydrous}]{FeCl_3}$ C_6H_5-Cl + HCl

(2) benzene + HCl + $\frac{1}{2}O_2$ $\longrightarrow$ C_6H_5Cl + H_2O

(3) 3 (anthraquinone sulfonate, SO_3Na) + $6HCl$ + $NaClO_3$ $\longrightarrow$ 3 (chloroanthraquinone, Cl) + $4NaCl$ + $3H_2SO_4$
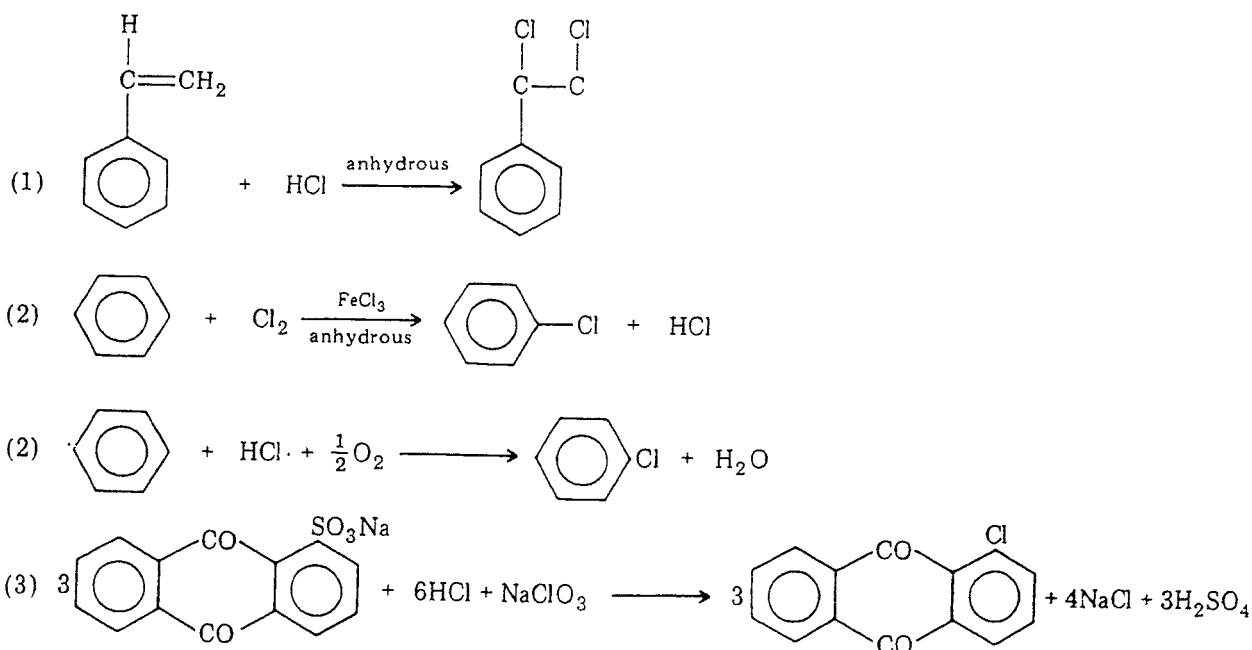
Reaction (3) can be run in hot, dilute, aqueous solution. Chlorinations are considerably less orderly than nitrations and sulfonations. Substitution rules are not as reliable since isomer distribution is influenced by hydrocarbon/chlorine ratios, and there is usually a considerable range of isomers formed. Light catalyzes some chlorinations, temperature has a profound effect, and polychlorination almost always occurs to some degree. All halogenations are strongly exothermic.

Equipment for chlorinations is more difficult to select than for most other unit processes. The combination of halogen, oxygen, halogen acid, water, and heat is particularly destructive to metals. A few alloys, such as Hastelloy and Durichlor, resist well, but they are expensive and difficult to machine. Glass, glass-enameled steel, and tantalum are totally resistant but not always affordable. Anhydrous conditions permit operation with steel or nickel alloys.

Technical Example of Chlorination. Chlorobenzene. Chlorobenzene enjoys a modest use as a solvent and for the manufacture of nitrochlorobenzenes. Its former uses for manufacturing phenol and aniline are gone. It is manufactured by passing dry chlorine through benzene using ferric chloride as a catalyst:

$$C_6H_6 + Cl_2 \xrightarrow{FeCl_3} C_6H_5Cl + HCl$$
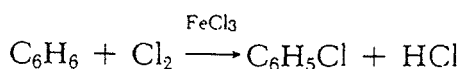
The reaction rates favor production of monochlorobenzene over dichlorobenzene by 8.5:1 providing that the temperature is maintained below 60°C. The HCl generated is washed free of chlorine with benzene, then absorbed in water. Distillation separates the monochlorobenzene, leaving mixed isomers of dichlorobenzene to be disposed of.

HYDROLYSIS. Replacement of $-SO_3H$ or $-Cl$ with $-OH$ is frequently desired and is usually accomplished by fusion with alkali. Polysubstituted molecules may be hydrolyzed with

less drastic conditions. Besides alkaline substances, hydrolysis is brought about by enzymes, acids, or sometimes water alone.

A typical reaction is:

$$ArSO_3Na \text{ (or ArCl)} + 2NaOH \rightarrow ArONa + Na_2SO_3 \text{ (or NaCl)} + H_2O$$

Acidification will give ArOH. SO_2 or CO_2 may be sufficiently acidic to "spring" the ArOH. Most hydrolysis reactions are modestly exothermic.

Cast iron or steel open fusion pots heated to the high temperatures required (200 to 325°C) with oil, electricity, Dowtherm, or quite commonly directly with gas, are standard equipment.

Examples of Technical Hydrolyses. Phenol was at one time made by the fusion of benzene sulfonic acid with caustic soda, but the present method via cumene is cheaper. The hydrolysis of chlorobenzene to phenol requires far more drastic conditions and is no longer competitive. Ethylene chlorohydrin can be hydrolyzed to glycol with aqueous sodium carbonate. Hydrolysis uses a far wider range of reagents and operating conditions than most of the previously discussed chemical conversion processes. Even at the present cost of electricity, a 750 J/s (1 HP) motor can be used for about four hours for the cost of 1 kg of NaOH, so great interest prevails in manufacturing for the substitution of energy for chemicals.

The following chemicals, many previously discussed, have hydrolysis involved in their manufacture:

Cellulose → glucose

Pentosans → furfural

Ethyl hydrogen sulfate → ethyl alcohol

Starch → glucose

Propane → glycerol

Fats → fatty acids + glycol

Aryl and alkyl halides → alcohol

Olefins → alcohols

ALKYLATION OF AMINES. Alkylation is usually used to increase the resistance of dyes to shade changes when exposed to dilute alkalis or acids. For example, dihydroxybenzanthrone is alkylkated with dimethyl sulfate to produce vat green 1. The usual alkylating agents for amines are varied but include alcohols, alkyl halides, dialkyl sulfates, and the methyl ester of *p*-toluenesulfonic acid. Jacketed autoclaves with stirrers and internal cooling coils are used, for some reactants are volatile and require pressure for containment.

Technical Example of Alkylation. Dimethylaniline. Dimethylaniline is employed in the manufacture of a number of triarylmethane dyes. It is prepared according to the reaction:

$$C_6H_5NH_2 + 2CH_3OH \xrightarrow{H_2SO_4} C_6H_5N(CH_3)_2 + 2H_2O$$
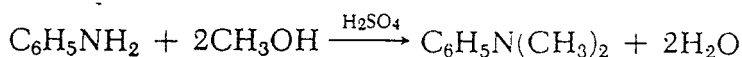
Aniline, with a considerable excess of methanol and a little sulfuric acid, is heated in an autoclave at about 200°C for 5 or 6 h. The pressure rises to around 3.7 MPa. Vacuum distillation is used for purification.

OXIDATION.[10] Control is the major problem where oxidation is practiced. Only partial oxidation is wanted as one organic compound is converted into another. It is simple enough to

[10]Groggins, op. cit., chap. 9; Sittig, *Combining Oxygen and Hydrocarbons for Profit*, Gulf, Houston, Tex., 1962.

make CO_2 and H_2O from organic substances, but once started, it is difficult to stop oxidation before it is completed. The commonest reagent is air, but oxygen frequently proves to be less expensive. The chemical oxidizing agents, nitric acid, dichromates, permanganates, chromic anhydride, chlorates, and hydrogen peroxide, are usually an order of magnitude more expensive than the gases, so they are employed only when the gases do not function well. The combustion reaction is extremely exothermic:

$$H_2 + \tfrac{1}{2}O_2 \rightarrow H_2O \qquad \Delta H = -2.41 \text{ MJ}$$
$$C + O_2 \rightarrow CO_2 \qquad \Delta H = -2.85 \text{ MJ}$$
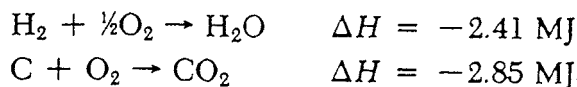
Since some complete combustion always accompanies partial oxidation, heat removal is frequently the controlling factor in oxidations.

Technical Example of Oxidation. Phthalic acids and anhydride, produced primarily from xylenes, are used in the manufacture of several dyes, plastics, and plasticizers. Their production is covered in Chap. 34. The anhydride is converted to anthraquinone, to phthalocyanines, and phenolphthalein, along with several other derivatives. Phenol (Chap. 34) is also made from cumene by oxidation. These two substances have become so widely used that the part going into dyes has become almost trivial.

CONDENSATION AND ADDITION REACTIONS (FRIEDEL-CRAFTS). There are only a few products manufactured in any considerable tonnage by these reactions, but those which are find use in several different intermediates and particularly in making high-quality vat dyes. The agent employed in this reaction is usually an acid chloride or anhydride, catalyzed with aluminum chloride. Phthalic anhydride reacts with chlorobenzene to give *p*-chlorobenzoylbenzoic acid:
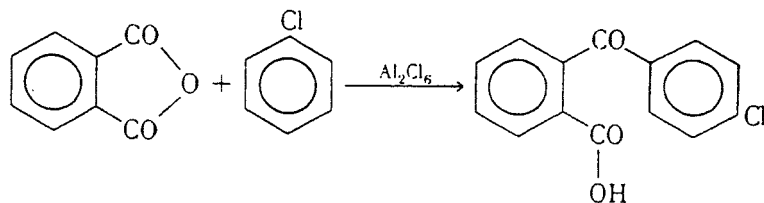
in a continuing action, the *p*-chlorobenzoylbenzoic acid forms β-chloroanthraquinone by ring closure.
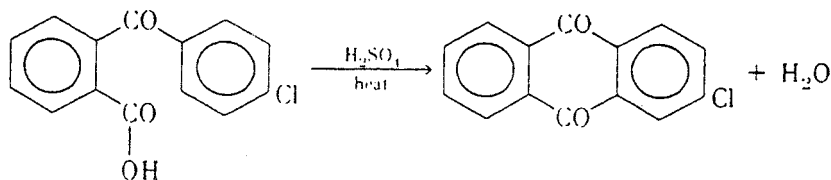
Since anthraquinone is a relatively rare and expensive component of coal tar and petroleum, this type of reaction has been the basis for making relatively inexpensive anthraquinone derivatives for use in making many fast dyes for cotton. A list[11] of important intermediates made using addition reactions is available.

Friedel-Craft reactions are highly corrosive, and the aluminum-containing residues are difficult to dispose of.

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[11]CPI 4, p. 727.

MISCELLANEOUS CONVERSIONS. Every reaction ever disclosed by an organic chemist is available and potentially valuable for the production of some intermediate. Among these are acylation, carboxylation, and ring closure. A list[12] of compounds made commercially by these less common processes is available.

DYES

Dyes add value to products far beyond their cost. Frequently the color of a product is the reason for its sale. Some dyes have special uses, such as radiation detectors and photosensitive dyes for papers and posters. The purpose of a dye is usually to help the purchaser sell his product to his customer. Dye sales in 1980 were estimated at $608 million. Every dye sale is estimated to influence $10 in product sales, so the effect is far greater than the cost. Typical dye molecules appear complicated and confusing, but their synthesis follows an orderly procedure, using about 1000 intermediates and comparatively few chemical conversions.

A dye must be colored, but it must also be able to impart color to something else on a reasonably permanent basis before it can be considered as a dye. Most dyes contain considerable unsaturation, and some part of the dye is usually in the form of aromatic rings with nitrogen unsaturation of several types common to many dyes. The quinoid structure appears frequently. The dye tree of Fig. 39.5 shows the development of several major dyes and their discovery dates. Obviously, the dye industry boomed when chemistry was in its infancy.

Many correlations have been made (and more attempted) between chemical structure and color. Color results from electronic transitions between molecular orbitals. Some early observations are still worth studying and are easier to comprehend than electronic structures. These concepts began to be used as early as 1876 and reached their present state about 1930.

A dye consists of a color-producing structure, the *chromogen* (electron acceptor), and a part to regulate the solubility and dyeing properties, the *auxochrome* (electron donor). Without both parts, the material is simply a colored body.

The chromogen is an aromatic body containing a color-giving group, commonly called the *chromophore*. Chromophore groups cause color by altering absorption bands in the visible spectrum. Common chromophores are:

1. The nitroso group: $-NO$ (or $=N-OH$)
2. The nitro group: $-NO_2$ (or $=NOOH$)
3. The azo group: $-N=N-$
4. The ethylene group: $>C=C<$
5. The carbonyl group: $>C=O$
6. The carbon-nitrogen groups: $>C=NH$ and $-CH=N-$
7. The carbon-sulfur groups: $>C=S$ and $\geqq C-S-S-C\leqq$

These groups add color to aromatic bodies by causing displacement of, or an appearance of, absorbent bands in the visible spectrum. The chromophore groups are the basis of one method of dye classification.

Some molecules lose their colors when the chromophore groups are saturated. The auxochromes, the part of the dye which causes it to adhere to the material which it colors (usually
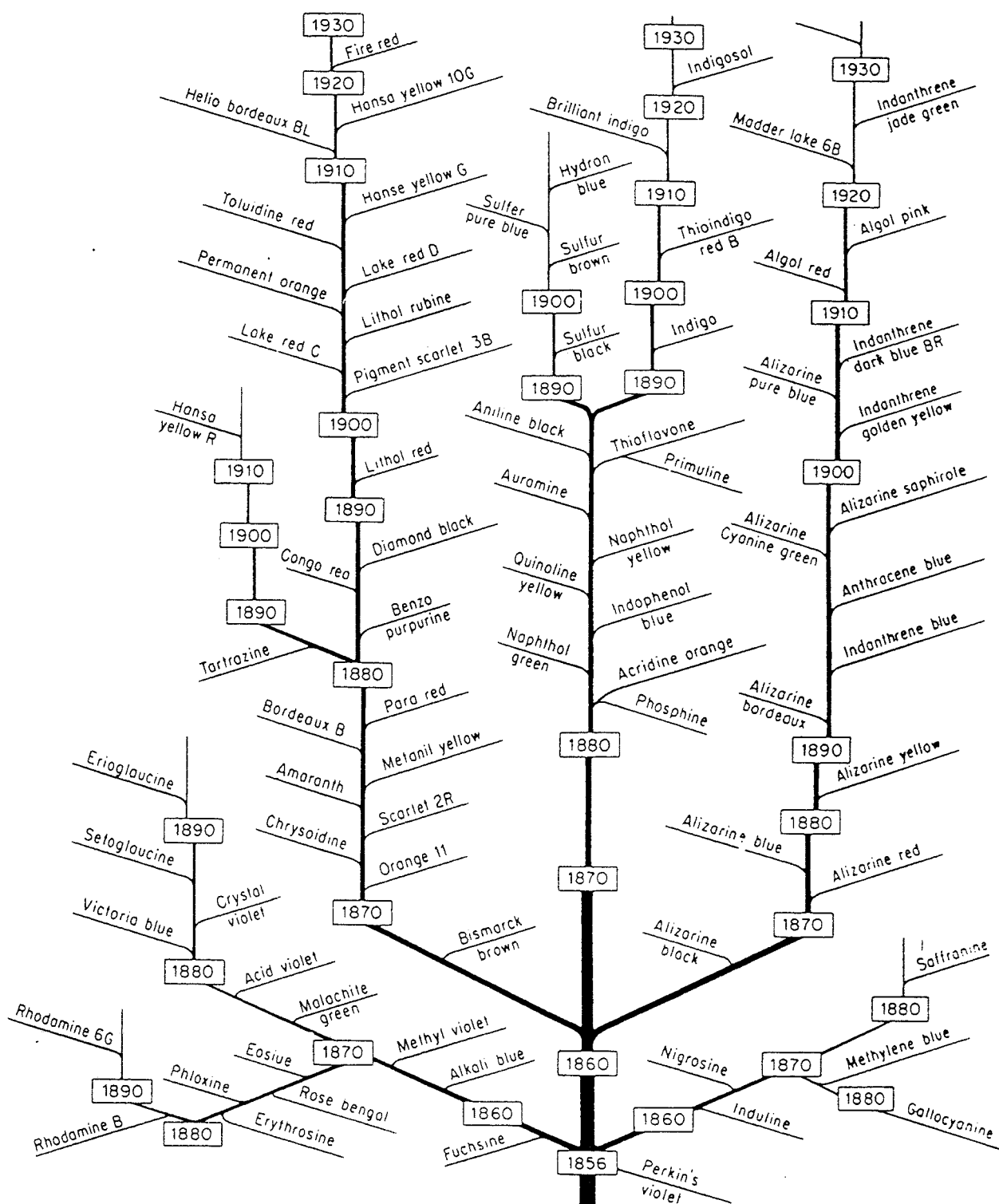
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[12]CPI 4, p. 728.

Fig. 39.5. Significant developments in organic color chemistry. *(Interchemical Corp. and John Wiley and Sons, Inc.)*

textiles), are: —NH₂, —OH, —NR₂, —COOH, and —SO₃H. It is not a coincidence that these are salt-forming materials; —NH₂ and —NR₂ cause solubility in acid; —OH, —COOH, and —SO₃H cause solubility in basic solutions.

Figures 39.6, 39.7, and 39.8 are helpful in visualizing the relationship between precursors, intermediates, and a few simple dyes.
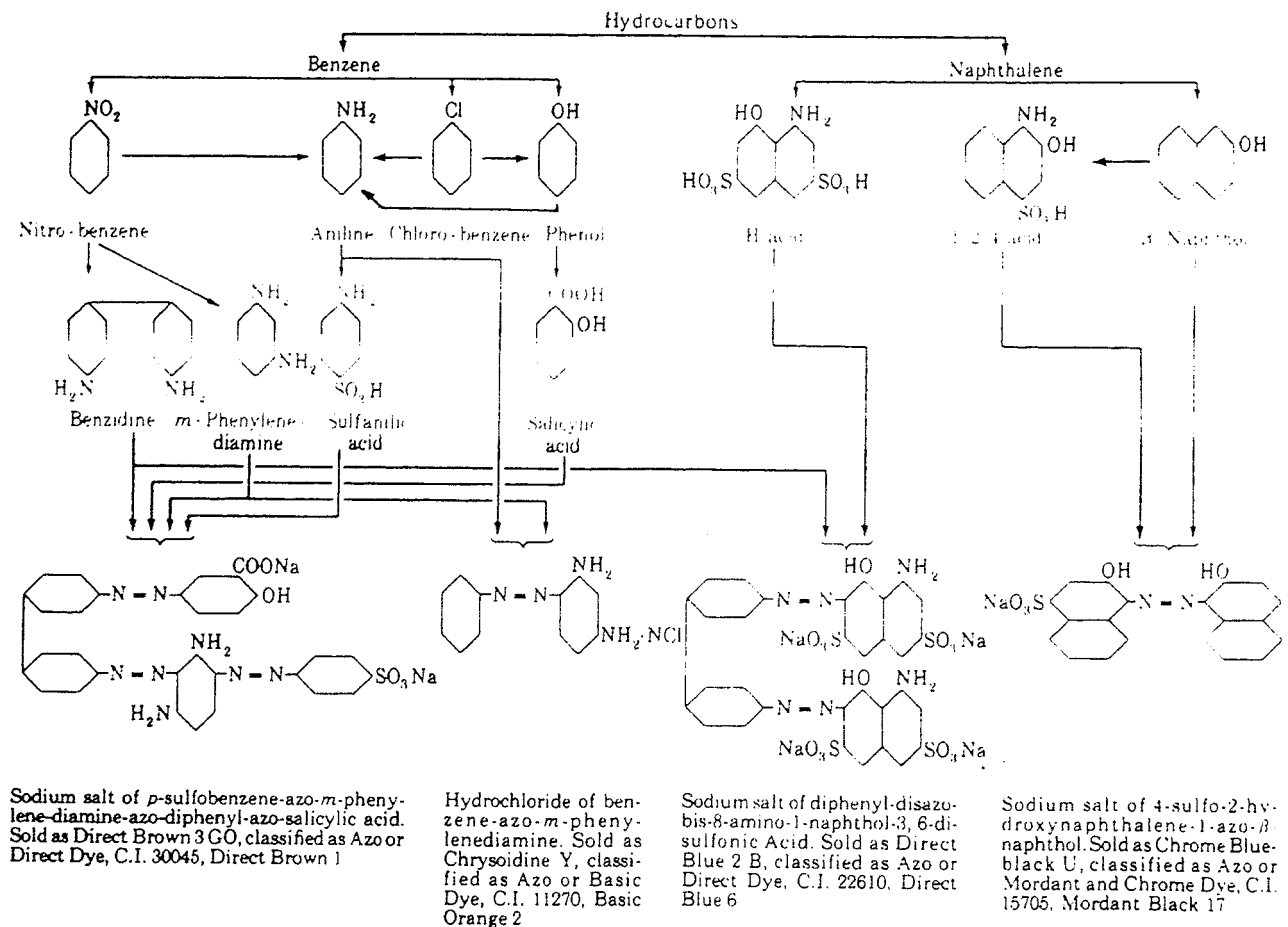
Hydrocarbons

Benzene

Naphthalene

Nitro-benzene

Aniline Chloro-benzene Phenol

H acid

Benzidine *m*-Phenylene- Sulfanilic
diamine acid

Salicylic
acid

Sodium salt of *p*-sulfobenzene-azo-*m*-pheny-lene-diamine-azo-diphenyl-azo-salicylic acid. Sold as Direct Brown 3 GO, classified as Azo or Direct Dye, C.I. 30045, Direct Brown 1

Hydrochloride of ben-zene-azo-*m*-pheny-lenediamine. Sold as Chrysoidine Y, classi-fied as Azo or Basic Dye, C.I. 11270, Basic Orange 2

Sodium salt of diphenyl-disazo-bis-8-amino-1-naphthol-3, 6-di-sulfonic Acid. Sold as Direct Blue 2 B, classified as Azo or Direct Dye, C.I. 22610, Direct Blue 6

Sodium salt of 4-sulfo-2-hy-droxynaphthalene-1-azo-β-naphthol. Sold as Chrome Blue-black U, classified as Azo or Mordant and Chrome Dye, C.I. 15705, Mordant Black 17

Fig. 39.6. Relationship of hydrocarbons, intermediates, and some azo dyes.

Petroleum or coal tar

Toluene

Benzene

Naphthalene

p-Nitro-toluene

o-Nitro-toluene

Nitro-benzene

β-Naphthol

p-Tolylenediamine

o-Toluidine

Aniline

Dimethyl-aniline

G acid

Diamino-phenyl-ditolazon-ium chloride. Sold as Safra-nine, classified as Azine or Basic Dye, C.I. 50240, Basic Red 2

Tetramethyl-diamino-diphenaz-thionium chloride. Sold as Methylene Blue, classified as Thiazine or Basic Dye, C.I. 52015, Basic Blue 9

Hydrochloride of pentamethyl-pararos-aniline. Sold as Methyl Violet, classified as Triarylmethane or Basic Dye, C.I. 42535, Basic Violet 1

Sodium salt of anhydride of tetramethyl-diamino-diphenyl-hydroxynaphthyl-carbinol-disulfonic acid. Sold as Wool Green S, classified as Triarylmethane or Acid Dye, C.I. 44090, Acid Green 50
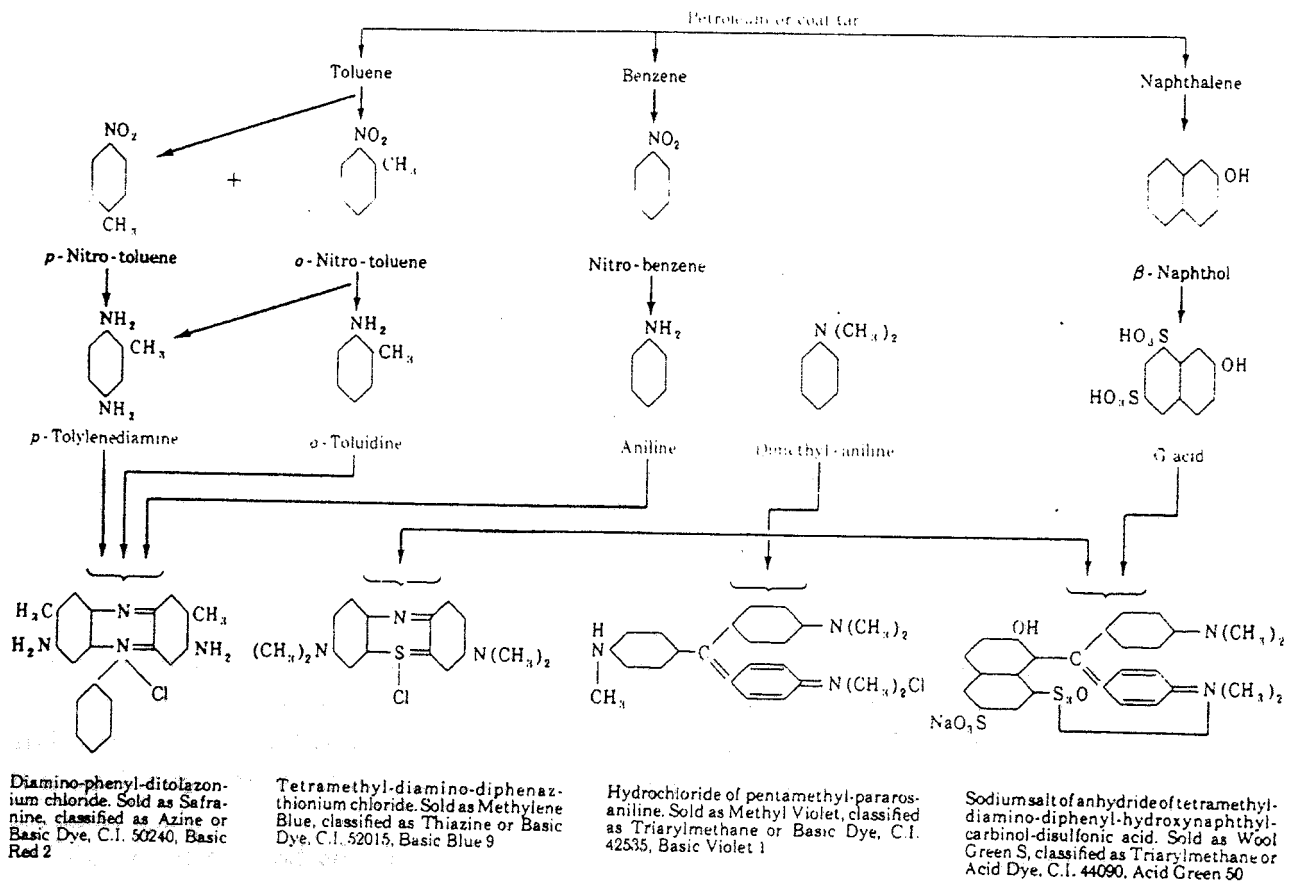
Fig. 39.7. Relationship of hydrocarbons, intermediates, and some azine, thiazine, and triarylmethane dyes.
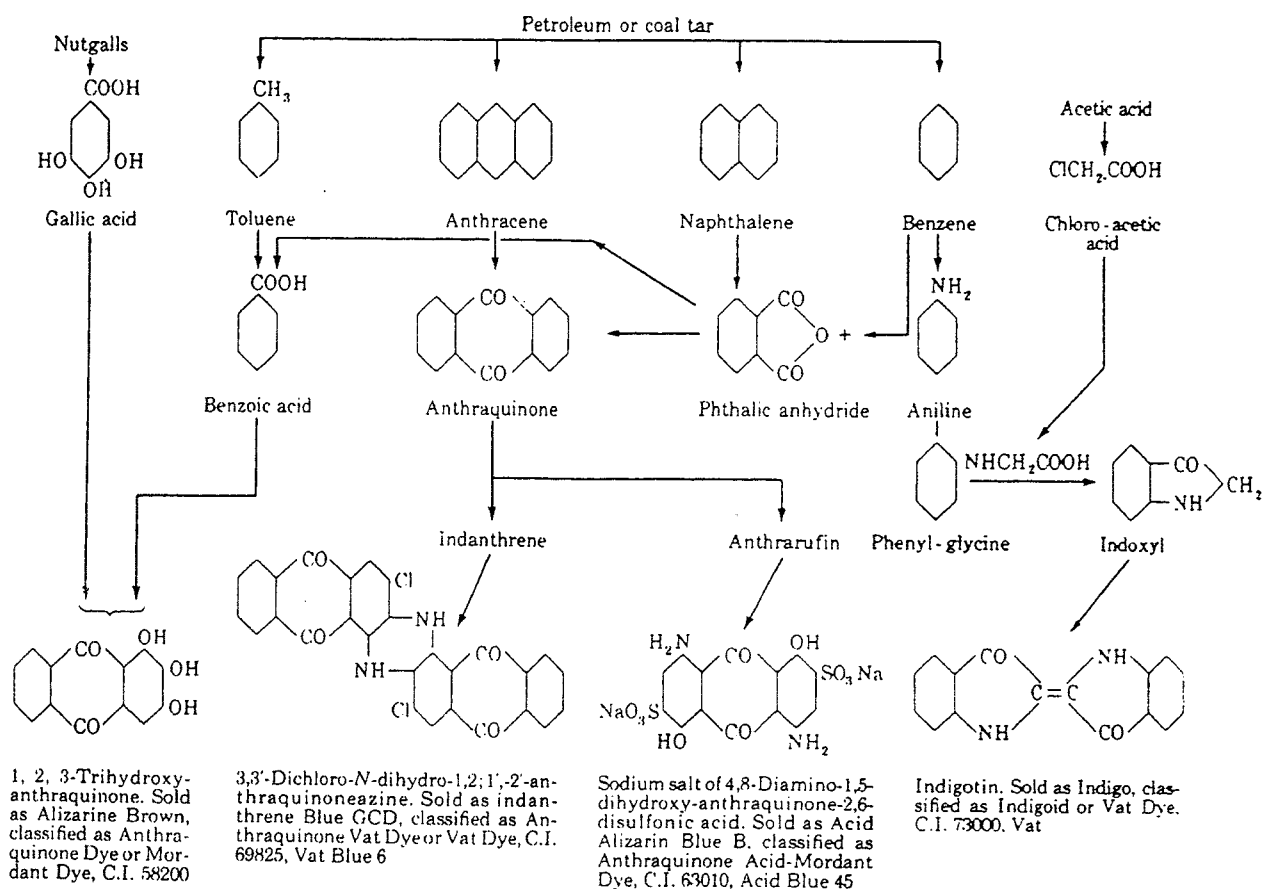
Fig. 39.8. Relationship of hydrocarbons, intermediates, indigo, and some anthraquinone dyes.

CLASSIFICATION OF DYES. It is possible to classify dyes by using an ingenious system[13] devised some years ago by the Society of Dyers and Colourists and published as the *Colour Index*. This is undoubtedly the most important book available concerning dyes. The *Colour Index* classifies dyes according to a dual system. An assigned number defines the chemical class and a generic name identifies the usage of application. Some manufacturers append a trivial or trade name. Notice in Figs. 39.6 and 39.9: Chrome blue-black U (a trade name), CI 15705 (Numbers 11,000 to 19,999 are reserved for monoazo dyes), Mordant black 17 (an azo dye applied as a mordant, No. 17 in the list of this type). The Colour Index recognizes 26 types of dyes by chemical classification: (1) nitroso, (2) nitro, (3) mono-, dis-, tris- and poly-azo, (4) azoic, (5) stilbene, (6) carotenoid, (7) diphenylmethane (ketone imine), (8) triaryl-methane, (9) xanthene, (10) acridine, (11) quinoline, (12) methine and polymethine, (13) thia-zole, (14) indamine and indophenol, (15) azine, (16) oxazine, (17) thiazine, (18) sulfur, (19) aminoketone, (20) hydroxyketone, (21) anthraquinone, (22) indigoid, (23) phthalocyanine, (24) natural organic coloring matters, (25) oxidation bases, and (26) inorganic coloring matters.

It is convenient to use the application classification used by the U.S. International Trade Commission for application classes: (1) acid dyes, (2) azoic dyes, (3) basic dyes, (4) direct dyes, (5) disperse dyes, (6) fiber-reactive dyes, (7) fluorescent brightening agents, (8) food, drug, and cosmetic colors, (9) mordant dyes, (10) solvent dyes, (11) sulfur dyes, and (12) vat dyes. It is obviously impractical in a book of this size to discuss all the combinations of properties

[13]*Colour Index*, 3d ed., 5 vols., Society of Dyers and Colourists, Bradford, England, and American Association of Textile Chemists and Colorists, Lowell, Mass., 1971.
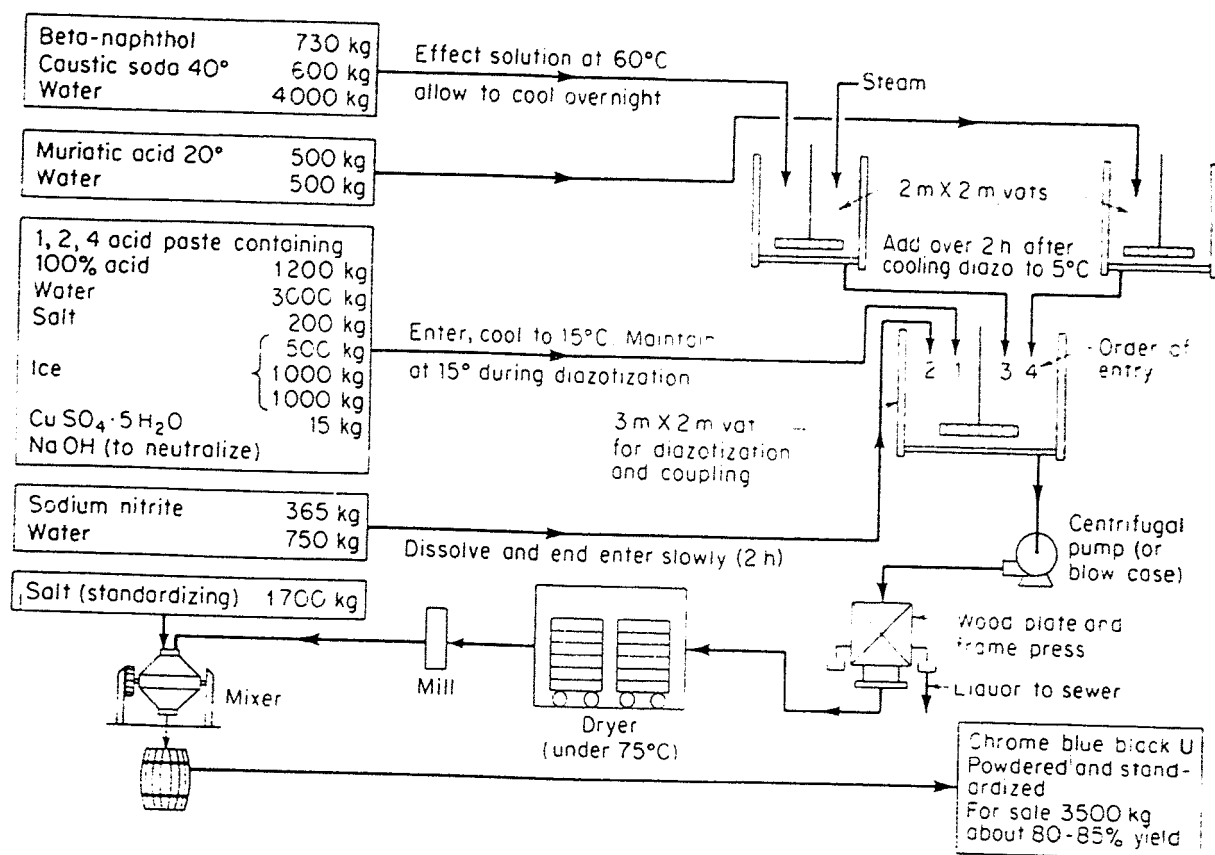
Fig. 39.9. Flowchart for Chrome Blue Black U, CI 15705, mordant black 17. A monoazo or chrome dye; batch = 5 kg-mol.

and chemical compositions possible. Note, however, that six classes form the bulk of the market, so it is possible to concentrate on them. Table 39.3 shows the size and value of the markets. They are: acid, basic, direct, disperse, reactive, and vat dyes. Large compendiums[14] make it possible to obtain data on those omitted here.

The significance of the various application classes are as follows:

Acid dyes. These derive their name from their insolubility in acid baths. They are used for dyeing protein fibers such as wool, silk, and nylon; also leather and paper. Usually they are azo, triaryl methane, or anthraquinone complexes.

Azoic dyes. These "ice colors" are made right on the fiber by coupling diazotized materials while in contact with the fibers. Low temperature keeps the diazonium compound from decomposing until ready to couple. These are brilliant and long-lasting and are used primarily for printing on cotton.

Basic dyes. Basic dyes are mostly amino and substituted amino compounds soluble in acid and made insoluble by the solution being made basic. Most are triarylmethane or xanthenes. These can be used to dye wool or cotton with a mordant, but are usually used for duplicator inks, carbon paper, and typewriter ribbons. In solvents other than water, they form writing and printing inks.

Direct dyes. Direct dyes are used to dye cotton directly, that is, without the addition of a mordant. They are also used to dye union goods (mixed cotton, and wool, or silk). These are generally azo dyes, and their solubility in the dye bath is often reduced by adding salt.

[14]Venkataraman, op. cit.; ECT, op. cit.; Kent, *Riegel's Industrial Chemistry*, Reinhold, New York, 1962.

Table 39.3 Comparison of U.S. Production of Dyes, by Classes of Application

Class of Application	1972 Production, 10^3 kg	1972 Value, 10^6 $	1980 Production, 10^3 kg	1980 Value, 10^6 $
Acid	13,518	71.7	11,640	115
Basic (classical and modified)	8,181	48.9	6,634	71.1
Direct	17,124	59.2	14,191	83.3
Disperse	18,149	107.6	21,236	178.1
Fiber reactive	1,681	15.6	2,605	36.0
Fluorescent brightening agents	12,419	38.3	17,245	60.4
Food, drug, and cosmetic colors	2,111	19.8	2,761	48.4
Mordant	666	2.6	186	1.9
Solvent	5,667	22.3	4,829	28.9
Vat	25,064	63.3	18,286	120.4
All others	10,461	16.3	11,909	46.9

SOURCE: *Synthetic Organic Chemicals*, U.S. International Trade Commission.

Some are developed on the fiber by forming the diazonium salt on the cloth, then coupling to increase insolubility. β-Naphthol is the most common developing agent.

Disperse dyes. Modern synthetics (cellulose acetate, plastics, polyesters) are difficult to dye. Disperse dyes are applied as very finely divided materials which are adsorbed onto the fibers with which they then form a solid solution. Simple, soluble azo dyes can be used, but insoluble anthraquinone colors are best and most common. Both penetrate the fiber. The ethanolamine group $-NHCH_2CH_2OH$ is commonly found in this group and aids both in dispersion and absorption.

Fiber-reactive dyes.[15] These dyes react to form a covalent link between the dye and the cellulosic fiber which they are customarily used to dye. This produces goods of outstanding wash-resistance. Cotton, rayon, and some nylons are dyed by this, the newest type of dyestuff to be invented (1956).

Fluorescent brightening agents.[16] Everyone knows what is meant by white, but its accurate definition and description prove to be quite elusive. "Bluing" has been used for a very long time to make yellowish laundry appear "whiter." Greater brilliance can be obtained with soap, textiles, plastics, paper, and detergents by the addition of these "optical brighteners." They absorb ultraviolet light and emit bright blues, which gives greatly improved whiteness. Brightners are stilbenes with some oxazoles and triazoles as well.

Reflecting pigments such as titanium dioxide are often added to paper to improve its whiteness. Brighteners are helpful in improving the appearance of recycled paper.

Food, drug, and cosmetic colors.[17] These currently consist of only 52 dyes, a carefully controlled group of materials regulated by the U.S. Food and Drug Administration. Purity and safety are rigidly monitored; some dyes are "listed" and some are "certified." Listed ones

[15]Hildebrand, Fiber Reactive Dyestuffs, *CHEMTECH* 8 (4) 224 (1978).

[16]Consumer Demand Spurs Brightener Use, *Chem. Eng. News* 43 (15) 37 (1965); Blanchard, Harper, Gautreaux, and Reid, Optical Brightener Adsorption by Polymer-Treated Fabrics, *CHEMTECH* 1 (3) 181 (1971).

[17]Greene, Food Dye Users See Red over FDA Color Bans, *Chem. Eng.* 84 (2) 84 (1977); These Colorants Can't Hurt You, *Chem. Week* 120 (17) 65 (1977).

have met safety standards; certified ones have the actual batch identical with an approved original standard. Considerable controversy surrounds several currently approved colors. and it seems probable that the number will be reduced still farther. An interesting development is the linking of certain dyes to polymer chains, thus causing them to pass through the digestive tract unchanged. Several such colors are currently undergoing tests to determine their chronic effects. Approved colors include anthraquinones, azos, and indigoids.

Mordant dyes (and lakes). Some dyes combine with metallic salts (mordant means bitter) to form highly insoluble colored materials called lakes. These materials are usually used as pigments. If a cloth made of cotton, wool, or other protein fiber is impregnated with an aluminum, chromium, or iron salt and then contacted with a lake-forming dye, the metallic precipitate forms in the fiber, and the colors become far more resistant to light and washing. Substituent groups such as $-OH$ and $-COOH$ attached to azo or anthraquinone nuclei are capable of reaction with metals to form mordant dyes.

Solvent dyes. Some simple dyes are soluble in alcohols. chlorinated hydrocarbon solvents, or liquid ammonia and there appears to be considerable promise in dyeing the difficult to dye synthetics, polyesters, polyacrylates, and triacetates, from such solutions. Perchloroethylene has been the preferred solvent to date. Such technology would greatly decrease the problem of removing unabsorbed dye from outfall waters. which can be very troublesome to dyers. The system has had some success in Europe. Because new dyeing machines must be developed to handle the volatile solvents used. and because the designs to contain the vapors represent considerable change from present machines. dyers in the United States have not shown a great deal of interest. Solvent, sometimes called spirit-soluble. dyes are usually azo, triarylmethane bases, or anthraquinones. They are used to color oils. waxes. varnishes, shoe polishes, lipsticks, and gasolines.

Sulfur dyes (sulfide dyes). These are a large, low-cost group of dyes which produce dull shades on cotton. They have good fastness to light. washing. and acids. but are very sensitive to chlorine or hypochlorite. The chromophore is complex and not well-defined; it is made by reacting sulfides and polysulfides with chlorinated aromatics. Sulfur dyes are usually colorless when in the reduced form in a sodium sulfide bath but gain color on oxidation. They have been used for a long time.

Vat dyes. These have chemical structures that are highly complex and most are derivatives of anthraquinone or indanthrene. On reduction in solution, they become alkali-soluble and colorless, and are called leuco vats. The colorless compounds are used to impregnate cotton fibers, which are then treated with an oxidant or exposed to air to develop the colors. Vat dyes are expensive, but are used for fabrics in severe service with frequent washing, such as men's shirts. Some vats are supplied as pastes for printing. The pastes contain sodium hydrosulfite and an aldehyde reducing agent. They can be printed on cloth. then developed by passing through an oxidizing bath containing sodium dichromate or perborate. The production of some vat dyes is described in Fig. 39.10.

The best known dye of the class is indigo, which has a fascinating history.[18] It was originally obtained from European woad or Indian indigo (and was for a time grown as a cash crop in the United States). It is now made synthetically, see Fig. 39.11, and is one of the most popular colors in the world. When used for dyeing wool, it makes dark (navy) shades with excellent fastness properties. As a dye for cotton denim, its lack of fastness seems to be prized as a fad. Several modified indigos, such as thioindigo, give very bright shades with good fastness when used on rayon.

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[18] Baumler, *A Century of Chemistry*, Econ Verlag, Dusseldorf, 1968.
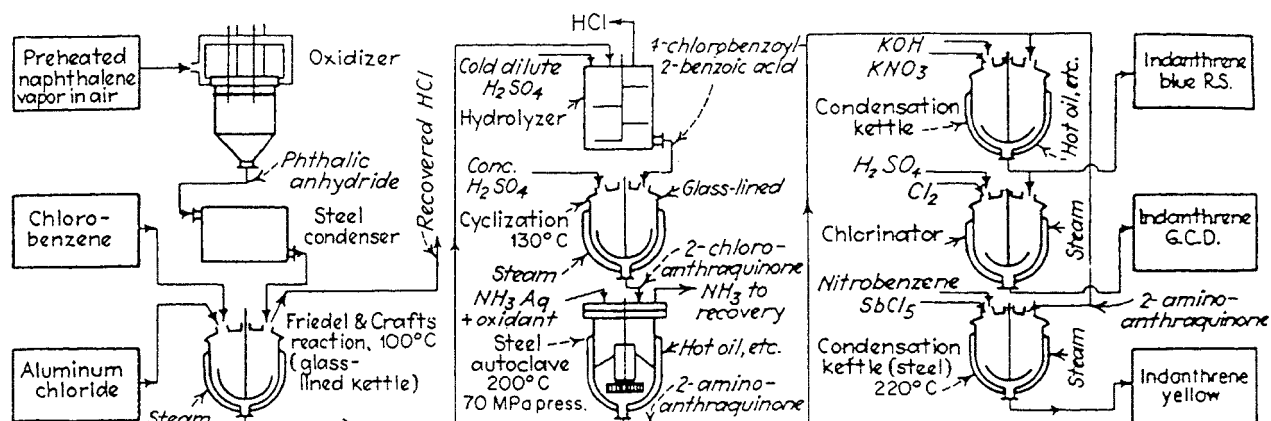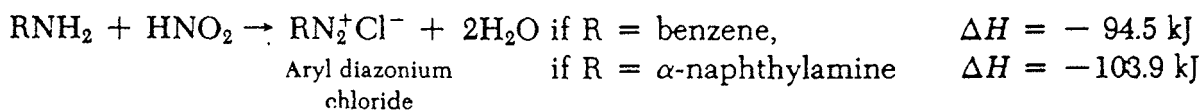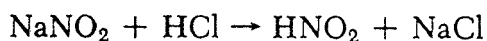
Materials (in kilograms) to produce simple vat dyes.

2-CHLOROANTHRAQUINONE, 235 KG		2-AMINOANTHRAQUINONE, 200 KG	
Phthalic anhydride	148	2-Chloroanthraquinone	235
Chlorobenzene (80% rec'd)	600	NH₃ (28%)†	1500
Aluminum chloride	300		
H₂SO₄ (100%)	1500		

INDANTHRENE YELLOW G, C.I. 70600, VAT YELLOW 2		INDANTHRENE BLUE R.S. C.I. 69800, VAT BLUE 4, 60–65 KG 100% DYE	
2-Aminoanthraquinone	200	2-aminoanthraquinone	200
Nitrobenzene°	2000	Caustic potash	1000
Antimony pentachloride	700	KNO₃ (or K-chlorate)	40

INDANTHRENE BLUE G.C.D., C.I. 69810, VAT BLUE 14, ABOUT 100% DYE

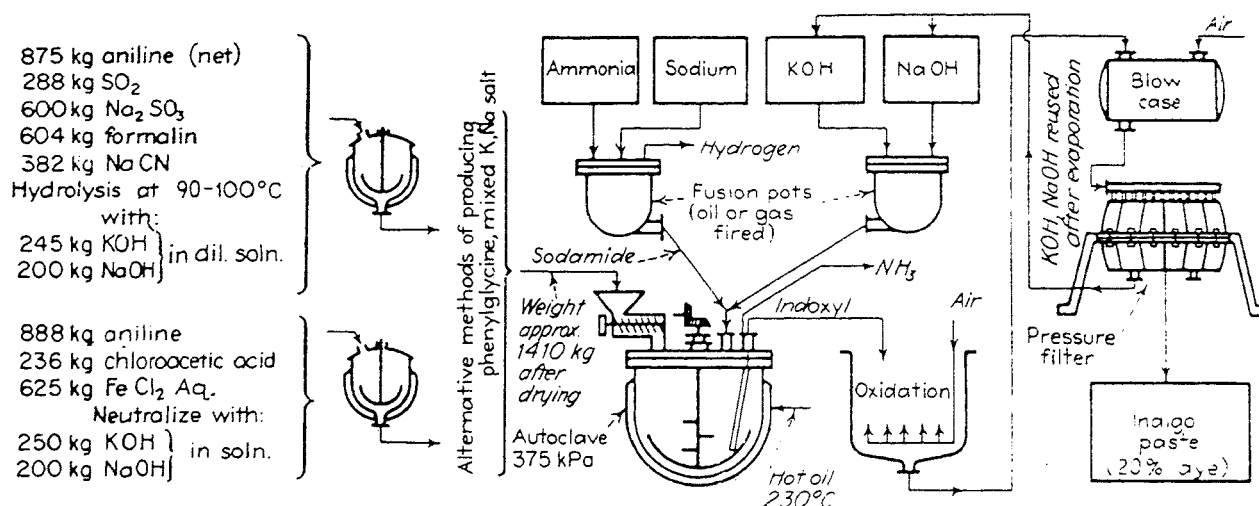| Indanthrene blue R.S.	100
H₂SO₄ (93%)	1200
FeSO₄	90
Cl₂	25

°Recovered as aniline or as nitrobenzene.
†90% recoverable.

Fig. 39.10. Outline flowchart for simple vat dyes, not detailed.

MANUFACTURE OF DYES. Because the chemistry is relatively easy (although the quality control is not) and so many reactions have small heat effects and can be run in simple open vessels, at one time many dyes were synthesized in wooden vats. The reaction between sodium nitrite and an amine, if carried out at ice temperature, produces a highly reactive ionized diazonium salt which will react (couple) rapidly with another molecule to form a body, which is usually colored, in nearly quantitative yield. Typical reactions are:

$$NaNO_2 + HCl \rightarrow HNO_2 + NaCl$$
$$RNH_2 + HNO_2 \rightarrow RN_2^+Cl^- + 2H_2O \text{ if } R = \text{benzene}, \qquad \Delta H = -94.5 \text{ kJ}$$
$$\text{Aryl diazonium} \qquad \text{if } R = \alpha\text{-naphthylamine} \qquad \Delta H = -103.9 \text{ kJ}$$
chloride

In order to produce 1 t of 100% indigo or 5 t 20% paste, the following materials (in kilograms) are required. NOTE: Yields 80–82 percent on aniline; KOH, NaOH, NH_3 recovered and reused.

| Phenylglycine (K,Na)	1550	Sodium	430
KOH (recovered)	1525	Ammonia	315
NaOH (recovered)	1200		

Fig. 39.11. Outline flowchart for the production of indigo.

COUPLING REACTIONS

$$RN_2^+Cl^- + ArOH \rightarrow RN=NArOH + HCl$$

$$\text{or } ArNH_2 \rightarrow RN=NArNH_2 + HCl$$
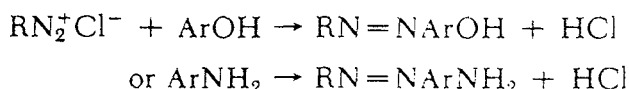
Coupling follows definite rules[19] determined by electronic configuration, and these permit isomeric structural differences to be exploited. Phenols, naphthols, and corresponding amines are the substances usually coupled. Polyfunctional intermediates can have nitro groups reduced after coupling and be coupled again. The pH of the bath may also determine the point of coupling. Consider the common intermediate, H-acid. (In the shorthand used for the naphthalene intermediates, known as NSSO 1368, S = SO_3H, N = NH_2, and O = OH, and the usual numbering system is used for the naphthalene.) It couples as follows:
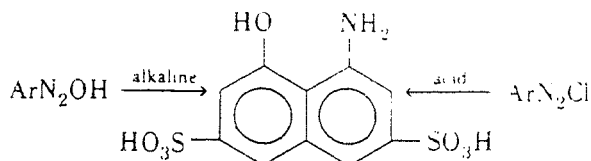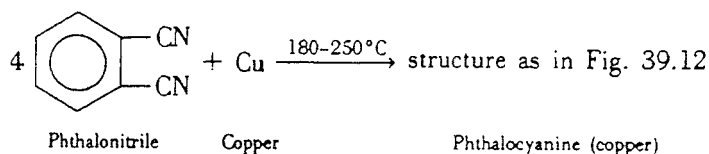

The wood vat has been almost entirely replaced by stainless steel, enameled steel, plastic, and rubber- and carbon-block–lined units, largely because of the ease of cleaning, which makes it unnecessary to reserve a vat for each color processed. There has also been a fair amount of automation, but Figs. 39.9 and 39.10 show typical steps in the manufacture of dyes. Great strides have been made in protecting the workers from toxic intermediates, increasing cleanliness as a whole, and standardizing colors for guaranteed reproducible

[19]Rys and Zollinger, *Fundamentals of the Chemistry and Application of Dyes*, Wiley, New York, 1972; Venkataraman, op. cit.; ECT, 3d ed., vol. 8, 1979, p. 159 ff; Abrahart; *Dyes and Their Intermediates*, Edward Arnold, London, 1977.

results. The industry still remains labor intensive, subject to abrupt changes in tastes for colors, and loaded with the burden of carrying a large inventory at a time of high interest rates. Customer service has also been a heavy load on the industry.

Complexity of dye structure does not necessarily indicate complexity of manufacture. Copper phthalocyanine (Fig. 39.12) is a good case in point. This is a highly chlorinated dye and is CI 74260, pigment green 7. There are 15 to 16 chlorine atoms, probably randomly distributed, per phthalocyanine unit. Phthalocyanines form only blues and greens, but their colors are extremely stable and give pigments used in artist's colors, printing inks, surface coatings, paper, floor coverings, and rubber. They are so stable that they have been used as high-temperature lubricants for space vehicles. They are made as follows:

$$4 \quad \text{(Phthalonitrile)} \xrightarrow[\text{Copper}]{+ \text{Cu} \quad 180\text{--}250\,°C} \text{structure as in Fig. 39.12}$$

Phthalonitrile   Copper   Phthalocyanine (copper)

NATURAL DYES. Most early dyes were animal-derived or vegetable extractives. Madder, indigo, Turkey red, Tyrian purple, picric acid, butternut juice, and walnut juice are some dyes known before chemistry took over, and some of them are quite good, but the good ones are usually extremely expensive to produce and quality control is virtually nonexistent. All extractives have disappeared from commercial use except logwood, CI 75290, natural black 1, which is the extract from the wood of a Central American tree.
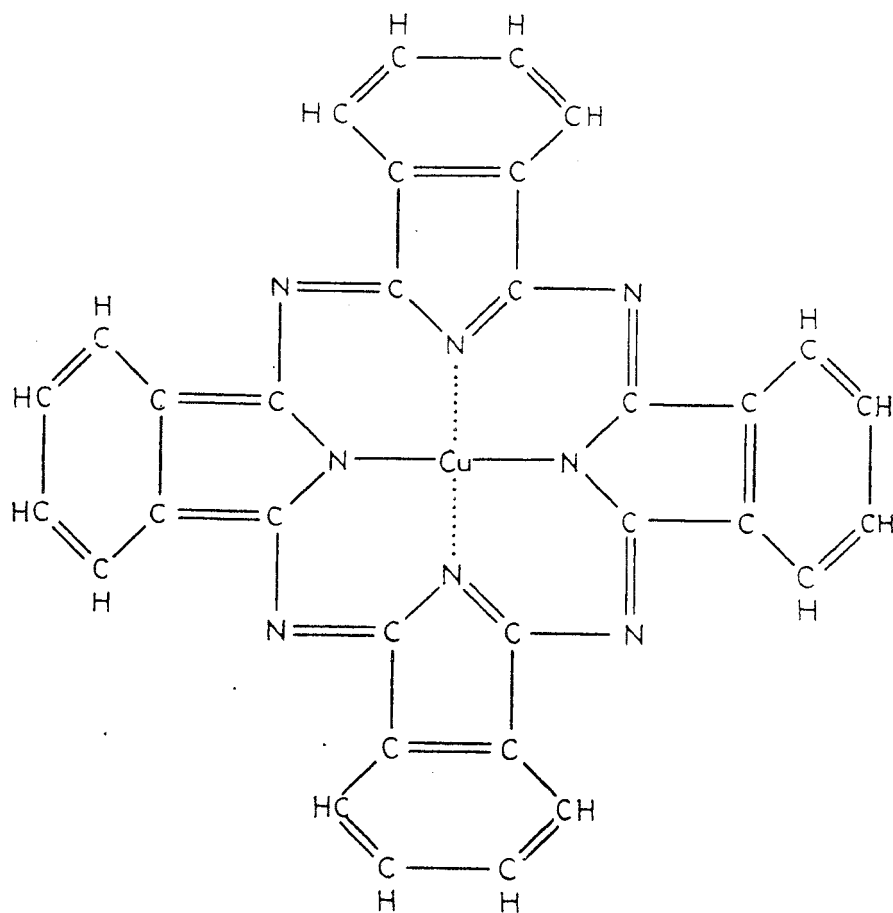

Fig. 39.12. Copper phthalocyanine basic structure.

INORGANIC COLORING MATTERS. Inorganic materials used as pigments are considered in Chap. 24. Some khaki for tents and similar outdoor use is still made by soaking the cloth in ferrous sulfate or acetate. On drying, or the addition of an alkali, the hydroxide is formed, which is oxidized to the more highly colored ferric hydroxide with bleach.

SELECTED REFERENCES

Abrahart, E. N.: *Dyes and Their Intermediates*, 2d ed., Chemical Publ. Co., New York, 1977.

Colour Index, 3d ed., 5 vols., Society of Dyers and Colourists, Bradford, England, and American Association of Textile Chemists and Colorists, Lowell, Mass., 1971.

Gurr, E.: *Synthetic Dyes in Biology, Medicine, and Chemicals*, Academic, New York, 1971.

James, R. W.: *Printing and Dyeing of Fabrics and Plastics*, Noyes, Park Ridge, N.J., 1974.

Johnston, R. M. and M. Saltzman (eds.): *Industrial Color Technology*, ACS, Columbus, Ohio, 1972.

Kirk, R. E. and D. F. Othmer: *Encyclopedia of Chemical Technology*, 3d ed., vol. 8, Wiley-Interscience, New York, 1979.

Lubs, H. A. (ed.): *The Chemistry of Synthetic Dyes and Pigments*, ACS Monograph No. 127, 1955.

Markakis, P.: *Anthocyanins as Food Colors*, Academic, New York, 1982.

Moser, F. H. and A. L. Thomas: *Phthalocyanine Compounds*, ACS Monograph 157, 1953.

Olin, A. D.: *Sources in Searching the Literature of Synthetic Dyes*, Tom's River Chemical Corp., Tom's River, N.J., 1963.

Rattie, I. D., and M. Breuer: *The Physical Chemistry of Dye Adsorption*, Academic, New York, 1974.

Rys, P. and H. Zollinger: *Fundamentals of the Chemistry and Application of Dyes*, Wiley-Interscience, New York, 1972.

Schmidlin, H. V.: *Preparation and Dyeing of Synthetic Fibres*, Reinhold, New York, 1963.

Tooley, P.: *Fuels, Explosives, and Dyestuffs*, J. Murray, London, 1971.

Venkataraman, K. (ed.): *The Chemistry of Synthetic Dyes*, several volumes, Academic, New York, 1952–1976.